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Elimination of the crystallinity of long polyethylene oxide-based copolymers for gas separation membranes by using electron beam irradiation

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Abstract:	PEO-based polymers containing long PEO chains are one of the best materials for post-combustion processes, attending to their separation properties. Optimal conditions for the application of the membrane separation module would be immediately after elimination of water vapor, NOx, SO2 and dust particles, where the temperature of the gas is between 25 and 40 °C., Materials with high contents and longer length of PEO would be the ideal candidate for the application in terms of properties. Unfortunately, these materials are normally not applicable due to, at these temperatures, the high crystallinity of PEO chains which leads to poor gas separation properties. Here, by electron beam irradiation, we have been able to eliminate or substantially reduce the crystallinity of poly(ether-imide)s with high content in PEO, which was confirmed by the positive effect in the separation properties. Optimal dosage to eliminate the crystallinity and to maximize permeability has been investigated as well.
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Please submit a plain text version of your cover letter here. Please note, if you are submitting a revision of your manuscript, there is an opportunity for you to provide your responses to the reviewers later; please do not add them to the cover letter.	September 14th, 2016 Dear Editor, I'm pleased to submit an original research article entitled "Elimination of the crystallinity of long polyethylene oxide-based copolymers for gas separation membranes by using electron beam irradiation" by Angel Marcos-Fernández, Esbaide Adem, A. Rubio Hernández-Sampelayo, Jose E. Báez, Laura Palacio, Pedro Prádanos, Alberto Tena, and Antonio Hernández for consideration for publication in Macromolecular Chemistry and Physics. PEO-based materials are considering the best materials for the application as a polymer membrane in post-combustion processes. Numerous research groups around the globe, having very high scientific community acceptance of their results, are working on it. Some of these research groups already assume that, in order to be applied, the future of this materials is only possible by the reduction or elimination of the high level of crystallinity normally presents on the materials (as for example recently Liu et. al. in Progress in Polymer Science 2013, 38, 1089). In this manuscript, we propose and experimentally prove the method which allows reduction and elimination of the crystallinity in PEO-based copolymers by electron beam irradiation. A rigorous treatment and characterization of the samples have been done in this very multidisciplinary and international work. Finally, the analysis of the separation properties confirms the crystallinity reduction effect, where the treated materials showed better separation properties than the original polymers. All this factors would favour the applicability of the PEO-based materials in important processes as post-combustion. We believe that this manuscript is appropriate for publication in Macromolecular Chemistry and Physics because it describes an innovative method for the elimination of the crystallinity in a really popular family of polymers that are applied in very diverse applications. The manuscript is completely original, and no part of it has been published and is not under consideration for publication elsewhere. This very international work was supported by several projects as DGAPA-PAPIIT-UNAM in México; or Ministry of Science and Innovation MAT2014-52644-R and Spanish Junta de Castilla y León VA-248U13, in Spain. We declare that we have no conflict of interest to disclose. Thank you for your consideration! Sincerely, Dr. Alberto Tena Institute of Polymer Research, Helmholtz-Zentrum Geesthacht Max-Planck-Str. 1 21502 Geesthacht, Germany Tel.: +49 4152 87 2448 Fax.: +49 4152 87 2466 E-mail: alberto.tena@hzg.de

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Elimination of the crystallinity of long polyethylene oxide-based copolymers for gas separation membranes by using electron beam irradiation.

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Abstract

PEO-based polymers containing long PEO chains are one of the best materials for *post*-combustion processes, attending to their separation properties. Optimal conditions for the application of the membrane separation module would be immediately after elimination of water vapor, NO_x, SO_2 and dust particles, where the temperature of the gas is between 25 and 40 °C. Materials with high contents and longer length of PEO would be the ideal candidates for the application in terms of properties. Unfortunately, these materials are normally not applicable due to,

at these temperatures, the high crystallinity of PEO chains, which leads to poor gas separation properties. Here, by electron beam irradiation, we have been able to eliminate or substantially reduce the crystallinity of poly(ether-imide)s with high PEO content , which was confirmed by the positive effect in the separation properties. Optimal dosage to eliminate the crystallinity and to maximize permeability has been investigated.

1. Introduction

Gas separation membranes of polyethylene oxide (PEO) based materials are very interesting for processes where the carbon dioxide is involved, such as pre- and post-combustion processes, because of their excellent performance for CO_2 removal. PEO consists of polar ether groups, which can produce quadrupole interactions with CO_2. It leads to the known high affinity of PEO towards CO_2. Eventually, it contributes to a higher selectivity during the gas separation process[1].

Long PEO chains can crystallize, and crystallinity has an enormous influence in the properties of the materials including their gas separation properties since crystals are non-permeable entities[1]. PEO crystals have a relatively low melting temperature, below 76 °C[2]. Using PEO-containing materials at temperatures above PEO melting point would be enough to have it in amorphous state. In the case of gas separation membranes, the permeability of the PEO-based materials would increase, but the selectivity is also affected by the temperature, and typically it would be strongly reduced. As an example, commercial PEBAX or Polyactive® polymers have selectivities close to 60 at 20 °C for the CO_2/N_2 pair, while at 50 °C the selectivity is almost halved[3, 4]. Therefore, lower temperatures during the process will result in lower permeabilities but higher selectivities, which is crucial to have a better separation factor and to reduce membrane area[5]. In the post-combustion process, in general, there is an initial step where the gas is cooled in order to remove most of the water vapor, NO_x, SO_2 and dust particles [5, 6]. After this step, the gas is ready to pass through the membrane at temperatures between 25 and 40 °C and any subsequent heating step would be

energetically inefficient. Thus, as already mentioned by Liu et al.[7], the reduction of the crystallinity of the PEO-based polymers is a critical point for the development and applicability of these polymers as gas separation membranes. In addition, PEO has a poor mechanical strength that has to be improved in PEO based materials in order to find industrial applications.

Various strategies have been considered to overcome these drawbacks (high crystallization tendency and a weak mechanical strength) in PEO: structural design of polymers via copolymerization, physical blending with other polymers and crosslinking, among others. The combination of PEO chains with poly(propylene oxide)[8], poly(dimethyl siloxane)[9]or other alkyl groups[10] have proved to reduce crystallinity and increase permeability in the polymers. When PEO is copolymerized with other monomers that react to form rigid segments (aromatic polyimide segments for example), a high selectivity is obtained almost regardless of the composition of the rigid segments[11-13]. With respect to the permeability, several parameters have been studied [7], and it was found that the main parameters where the content and the chain length of the PEO segments in the polymer[14, 15]. In general, higher content generates a continuous PEO phase which favors the permeability[16], and higher chain length promotes richer polyether areas, which favors the diffusion of the gas through the polymer[12, 17].

Incorporation of short PEO chains as an additive by physical blending improves permeability and reduces crystallinity of the samples[18, 19], but because there is not a covalent bond between the polymer matrix and the PEO short chains, a leaching of the later takes place and separation properties are worsened with time[20].

With crosslinking, the inter-polymer chain spacing is modified and therefore it can be used to quantitatively affect the free volume in the resultant network. Most of the PEO crosslinked gas separation membranes have been built from PEO oligomers with (meth)acrylate chain ends that polymerize to form a network[21-24]. For these systems, the chemical composition of the crosslinker

plays an important role in modifying the gas transport properties of the polymers. In general, these highly-rubbery crosslinked structures presented high CO_2 permeability values and good values for the separation CO_2/H_2 with special interest in the case of elevated feed pressures[25, 26], but the results for the separation CO_2/N_2 are not so high (high-selective materials are required for this separation). Another approach was the crosslinking of polymers with PEO chains, as for example the crosslinking of Matrimid with amine terminated PEO[27]. For this system, PEO length was critical, thus, a 2000 $g \cdot mol^{-1}$ molecular weight gave good gas separation results whereas a 600 $g \cdot mol^{-1}$ molecular weight was not suitable due to the poor mechanical strength of the membrane[28].

So far, to our knowledge, ionizing radiation has not been considered as crosslinking agent for PEO based gas separation membranes. Linear pure PEO has been already crosslinked by using ionizing radiation (gamma rays, electron beam), mainly for the production of hydrogels for biomedical applications[29-32], but also for the preparation of a dry polymer electrolyte in a lithium ion battery[33].

Ionizing radiation is known to produce changes in polymers such as scission, crosslinking and oxidation of polymer chains[34]. A FDA study concluded that all types of ionizing radiation (electron beam, gamma rays and X-ray) treatments were equivalents in terms of the type and levels of radiolysis products generated during irradiation[35]. It has been shown that when linear pure PEO was crosslinked with ionizing radiation in water or methanol solutions, both crosslinking and chain scission took place[31, 36, 37]. Gel content was slightly dependent on the molecular weight of the linear PEO with final gel content values in between 60 and 80%[28,30]. The minimum dose for the formation of a PEO gel in water solution, when irradiated with gamma rays, was found to increase with the increase in PEO concentration and a final value of approximately 100 kGy was needed at 25 °C for 100% pure linear PEO of 14400 $g \cdot mol^{-1}$ molecular weight. This value was slightly lower when irradiation was carried out at 80 °C[34].

In our previous work with PEO based copoly(ether-imide)s membranes, the best gas separation results were attained for copolymers with a good phase-separated morphology (achieved through thermal treatment) and long PEO chains[38, 39]. However, long PEO chains crystallized substantially reducing permeability and permeation measurements had to be performed at temperatures above the melting point of PEO chains. An increment in temperature leads to an increase in the permeability but decrease in the selectivity[12, 39].

In this work, electron beam irradiation was applied to copoly(ether-imide)s with long PEO chains (6000 g·mol^{-1}) to reduce and ultimately suppress PEO crystallinity in a simple way without affecting the chemical structure and the morphology of the copolymer. The effect of the absorbed dose in the thermal properties and its relationship with the gas separation properties were studied.

2. Experimental

2.1. Synthesis of copoly(ether-imide)s

The copoly(ether-imide)s used here were prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BKDA), polyoxyethylene-bis(amine) with nominal molecular weight of 6000 g·mol^{-1} (PEO6000) and 4,4'-oxydianiline (ODA). The diamines PEO6000 and ODA were reacted in weight ratios 2:1, 4:1 and 6:1 with BKDA giving a polyoxyethylene weight content in the final polymer of 44.2, 60.4 and 68.9% respectively. The resulting copoly(ether-imide)s (see chemical structure in Table 1) were designated PEO-44, PEO-60 and PEO-69 respectively according to the weight content of polyethylene oxide in the copolymers. The synthesis of the polymers and the film preparation are described in Marcos-Fernández *et al.*[40]. Before irradiation, films were thermally treated at 220 °C for 30 minutes to improve phase separation of the polyether and the polyimide blocks.

2.2. Electron beam irradiation

Samples with different dimensions were treated by electron beam irradiation. They were introduced into 9 cm x 6 cm polyethylene bags and placed in a holder for heating to 70 ºC. The device was specially designed and purpose built at the Institute of Physics, UNAM. The samples were irradiated at 70 ºC with an electron-beam accelerator, using a Van de Graaff source, 1.3MeVenergy and a beam current of 5 μA at a dose rate of 23.6 $kGy \cdot min^{-1}$. Doses covered the range 50–16000 kGy in air.

2.3. Characterization methods

For calorimetric studies, disc samples of 6 mm diameter were cut from the films. Differential scanning calorimetry (DSC) analyses were carried out in a Mettler Toledo (DSC 822e) calorimeter equipped with a liquid nitrogen accessory. Disc samples weighing 5–15 mg were sealed in aluminum pans. Samples were heated with the following method: from 25 ºC to 80 ºC at 10 $ºC \cdot min^{-1}$; from 80 ºC to -90 ºC at the maximum cooling rate accessible for the instrument; isotherm at -90 ºC for 10 min; from -90 ºC to 80 ºC at 10 $ºC \cdot min^{-1}$. All scans were carried out under a constant nitrogen purge. The melting point (T_m) is given as the maximum of the endothermic transition. Glass transition temperature (T_g) is given as the midpoint of the change in heat capacity. The percent of crystallinity of the PEO (X_c) respect to the PEO content in the copolymer was calculated from the endothermic peak area ΔHc corrected to the amount of PEO in the copolymer using the following equation: $X_c=(\Delta H_c/\Delta H_0)\cdot 100$, where ΔH_0 is the melting enthalpy of PEO taken from literature as 8.67 $kJ \cdot mol^{-1}$[41].

2.4. Gas permeation and selectivity

He, O_2, N_2, CH_4 and CO_2 permeabilities were measured by using a barometric constant volume permeator and the *time-lag* operation method. Measurements were carried out at 30 ºC and 50 ºC and the applied pressure was 3 bar. A sketch of the device used has been shown elsewhere[42]. Disc samples of 24 mm diameter cut from the films were used.

The strategy known as *time-lag* method, attributed to Daynes *et al*.[43], is very appropriate to determine permeability, diffusivity and solubility of a sample by a simple, rapid and accurate method working under transitory regime. The method has been successfully applied to determine polymer gas permeation by many authors[44, 45]. Its theoretical framework along with its practical possibilities and limits have been abundantly documented[46].

The transient response downstream the membrane to a pressure step enables the time-lag, t_0, to be easily computed. This parameter can be put, in terms of the diffusion coefficient, D, and the thickness of the membrane Δx, as:

$$t_0 = \frac{\Delta x^2}{6D} \quad (1)$$

The amount of gas transmitted at time *t* through the membrane is calculated from the permeate pressure readings in the low-pressure side. The permeability coefficient can be obtained directly from the flow rate into the downstream volume upon reaching the steady state. Solubility, S, can be obtained from directly measured diffusivities and permeabilities as follows:

$$S = \frac{P}{D} \quad (2)$$

The ideal selectivity can be defined as the ratio of pure gas permeabilities for each pair of gases.

3. Results and discussion

3.1. Calorimetric studies

Changes in thermal properties with dose (0, 50, 100, 150, 200, 300, 500, 1000, 2000, 4000, 6000, 8000, 10000, 12000, 16000 kGy) were measured by DSC. For some doses several samples were tested to estimate the dispersion of the results. It has already been demonstrated that these copoly(ether-imide)s present a phase separated structure with a PEO rich phase that can crystallize

partially and a totally amorphous polyimide rich phase with a T_g at high temperature[40]. In the first heating run, from ambient temperature to 80 ºC, an endothermic peak related to the melting of PEO crystals was found. After cooling, in the second heating run from -90 to 80 ºC, a T_g was observed at low temperatures (in some samples it could not be detected) for the amorphous PEO chains and an endothermic peak related to the melting of PEO crystals at higher temperatures. The values for PEO Tm and Xc from the first heating run and Tg from the second heating run for the copoly(ether-imide)s after irradiation at different doses are listed in Table 1.

In Figure 1, the percentage of crystallized PEO (after irradiation at 70 ºC with the PEO segments melted) *versus* dose is represented. PEO segments can crystallize in a very low proportion in the copolymer PEO-44 whereas PEO can crystallize extensively from the melt before irradiation in the copolymers PEO-60 and PEO-69. Crystallization is slightly higher for the copolymer PEO-69 that has a higher amount of PEO in its structure. PEO crystallinity decreased almost linearly with the increase in dose for all the copolymers until complete suppression of the crystallinity.

Ionizing radiation produces simultaneously chain scission and crosslinking on polymers, and the relative weight of each mechanism depends on the polymer structure[34]. If chain scission was predominant, it would be expected that the shorter PEO chains produced would have more mobility and could crystallize more easily, giving a higher amount of crystallized PEO. If crosslinking was predominant, chain mobility would be reduced and crystallization would decrease, as found for these copolymers.

The changes in the T_g value confirmed that crosslinking was the main mechanism present. This result is in agreement with the results found for pure PEO for which gel contents of 60-80% are obtained after irradiation in solution[28,30]. As it can be seen in Figure 2, initially the T_g value was practically constant for PEO-44 up to 2000 kGy, and for PEO-60 and PEO-69 decreased slightly with dose until a value of approximately 4000 kGy. Above these doses, the PEO is

completely amorphous in the materials and T_g value increased almost linearly with the increase in dose due to the movement restrictions imposed by the crosslinking.

In Figures 3 and 4, the maximum of the melting endotherm of PEO segments and the calculated amount of crystallized PEO respectively in the second heating run, are shown. The temperature of the maximum of the melting endotherm decreased monotonically with the increase in the absorbed dose for all the copolymers. Similarly to the first heating run, the amount of crystallized PEO decreased almost linearly with the increase in dose for all the copolymers until complete suppression of the crystallinity at 4000 kGy for copolymer PEO-44, at 6000 kGy for copolymer PEO-60 and at 8000 kGy (although it has almost disappeared at 6000 kGy) for copolymer PEO-69.

DSC results demonstrate that electron beam irradiation is effective on suppressing PEO crystallinity on these copoly(ether-imide)s with complete suppression at a dose of 6000 kGy and suppression of the crystallinity above ambient temperature at a dose of 4000 kGy.

3.2. Permeability test

Permeation tests were carried out in order to analyze the effect of the elimination of crystallinity by electron beam irradiation on the separation properties. In general, higher amount of PEO in the sample will increase the permeability of the samples[47]. In this sense, non-irradiated copolymer PEO-44 does not to show good gas permeation properties [39], thus permeation studies were not carried out on this material. Moreover PEO-69 was very fragile and the samples broke when loaded in the permeation cell, thus gas permeation was only evaluated in PEO-60 copolymers. The PEO crystallinity of the irradiated samples (X_c), calculated from the endotherm of the first DSC heating run, see Figures 1 and 2, is presented in Table 1. The values of the glass transition temperature, T_g, are also included.

The permeation experiments were carried out at two different temperatures: 30 ºC when there are some PEO crystals (for low absorbed doses) and 50 ºC when all PEO is in an amorphous state. He, O_2, CH_4,N_2 and CO_2 gases were tested. The CO_2/N_2 pair was analyzed in more detail due to it is the main mixture of gases to be separated in post-combustions processes.

Figure 5 shows the CO_2 permeability at 30 ºC as a function of the absorbed dose. CO_2 permeability increased until a maximum was reached and afterwards it decreased. The reduction on PEO crystallinity (see Figure 1) produced an increase on permeability but when PEO crystallinity was suppressed, and the increase in T_g (that is, the increase of the stiffness of PEO chains within the amorphous PEO phase) due to crosslinking hindered permeation and reduced permeability at 6000 kGy to a value similar to the non-irradiated sample. It is remarkable the increase of around 37% in the permeability in some cases. The elimination of the impermeable crystals from the copolymer produced an increase in permeability for all the gases tested[26].

The evolution of the carbon dioxide permeability at 50 ºC as a function of the absorbed dose was tested and it is showed in Figure 6. In this case the behavior is completely different. While at 30 ºC, it was observed an initial increase in permeability for increasing dose, now there is a continuous decrease of permeability when dose increases. Of course, for the permeability values at 30 °C, the initial increase of permeability was caused by the disappearance of the PEOcrystals. At 50 °C, the fundamental contribution that causes a decrease on the permeability is the increase on the PEO chains crosslinking produced by the increase in dose. Obviously, the mobility of the PEO chains is much lower, which reduces the diffusivity of the gas through the membrane.

The evolution of permeability versus the absorbed dose is similar for the other gases studied as shown for measurements performed at 30 ºC in Figure 7. Note that in all cases there are maxima within the range of 2000 to 4000 kGy.

Referring to selectivities, Figure 8 shows that there is not significant influence of the dose on the CO_2/N_2 selectivity. This is the case for the other pairs studied. These data confirm that the effect of irradiation is to reduce the PEO crystallinity and does not affect the rest of the structure. This behavior confirms the effectiveness of the irradiation treatment in the reduction of crystallinity; and shows how it is possible to control the properties of the material by irradiation. This would make possible using really large fragments of polyethylene oxide in copoly(ether-imide)s without the undesirable effects of crystallinity that otherwise would decrease permeability.

As mentioned, mobility of the chain segments increases permeability because straighter paths are accessible to each gas molecule. This reduces diffusive selectivity thus leaving as the main contribution to selectivity the differences in solubility, which is also reduced because some decrease in the internal surface should be expected. This leads to an experimentally confirmed decrease of permeability with permeability building the so called permeability-selectivity trade-offs that turned to be straights in a double log selectivity versus permeability plot (Robeson plots). In Figure 8 the upper bonds for the selectivity versus permeability trade-off are shown as fitted by Robeson[48] and as predicted for different temperatures by Rowe *et al*.[49]. Note that for permeation at 30 ºC and medium values of absorbed doses there is a nice increase in permeability without a significant loss in selectivity.

4. Conclusions

Irradiation with electrons of films made of copoly(ether-imide)s based on a long chain PEO of 6000 $g \cdot mol^{-1}$ produced an almost linear decrease in the PEO crystallinity until complete suppression, and an almost linear increase in the T_g value once PEO is completely amorphous, with the increase in dose. This behavior is consistent with crosslinking being the predominant mechanism over chain scission. Suppression of PEO crystallinity led to an increase in permeability

and, once PEO crystallinity disappeared, crosslinking of the amorphous PEO chains decreased permeability. Selectivity remained virtually constant with absorbed dose.

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Keywords:Polyethylene oxide, Electron beam irradiation, Crystallinity, Carbon dioxide (CO_2), Gas separation membrane

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Figure Caption

Figure 1. Percentage of crystallized PEO vs dose for the first heating run from ambient temperature for the copoly(ether-imide)s.

Figure 2. T_g vs dose for the copoly(ether-imide)s.

Figure 3. Maximum of the melting endotherm in the second heating run vs dose for the copoly(ether-imide)s.

Figure 4. Percentage of crystallized PEO vs dose for the second heating run for the copoly(ether-imide)s.

Figure 5. CO_2 permeability of the PEO-60 irradiated membranes as a function of absorbed dose measured at 30 ºC..

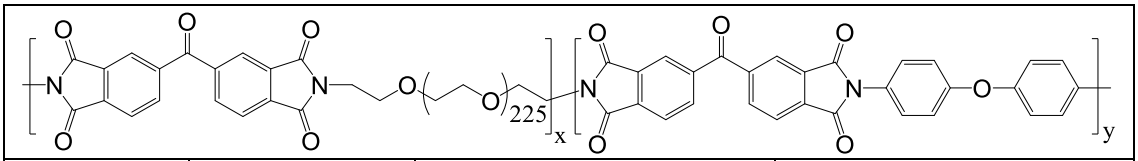
Figure 6. CO_2 permeability of the PEO-60 irradiated membranes as a function of absorbed dose measured at 50 ºC.

Figure 7. Permeabilities for other gases as a function of the absorbed dose for PEO-60.

Figure 8. Robeson plot for the CO_2/N_2 pair measured at 30 ºC (circles) and 50 ºC (squares).

Tables

Table 1. Percentage of crystallinity (Xc) from the first heating run and PEO glass transition temperature (Tg) from the second heating run for the copoly(ether-imide)s after irradiation at different doses.



Sample	Dose (kGy)	PEO Xc / % 1st heating	PEO Tg / °C 2nd heating
PEO-44	0	1.2	-60.6
	1000	0.2	-62.2
	2000	0	-61.5
	4000	0	-46.8
	6000	0	-36.6
PEO-60	0	37.1	-
	1000	22.0	-47.7
	2000	1.7	-56.0
	4000	0.9	-55.3
	6000	0	-49.0
PEO-49	0	433	-43.2
	1000	30.6	-45.7
	2000	8.5	-46.6
	4000	0.4	-52.7
	6000	0	-54.3

Figures

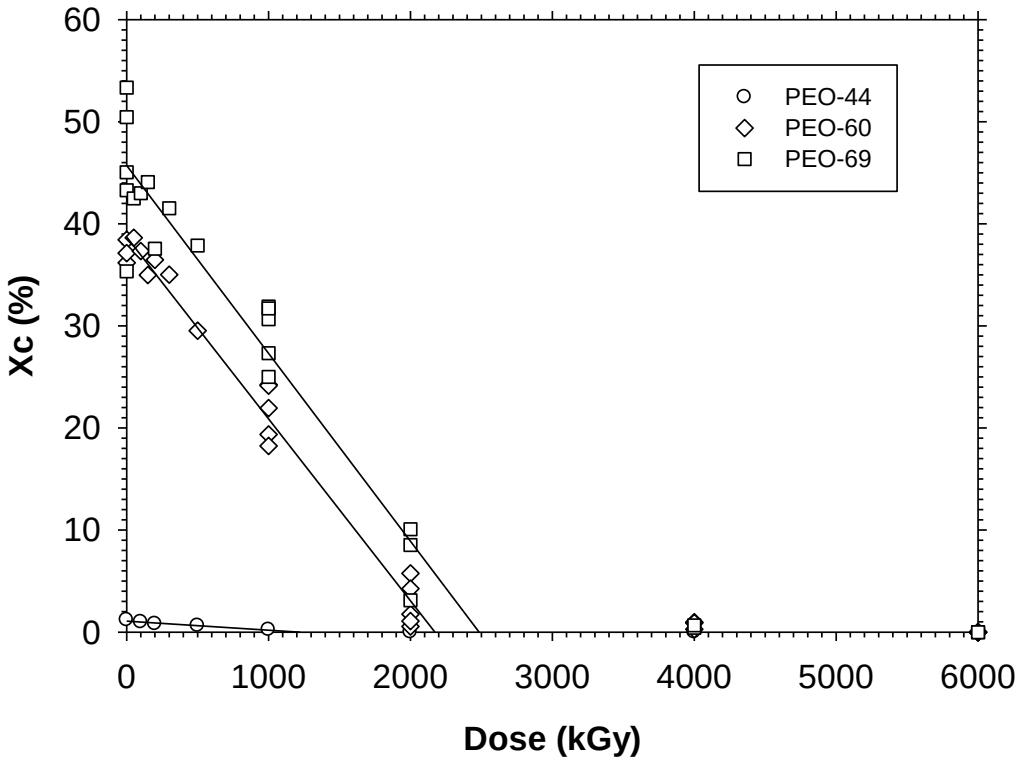


Figure 1. Percentage of crystallized PEO vs dose for the first heating run from ambient temperature for the copoly(ether-imide)s.

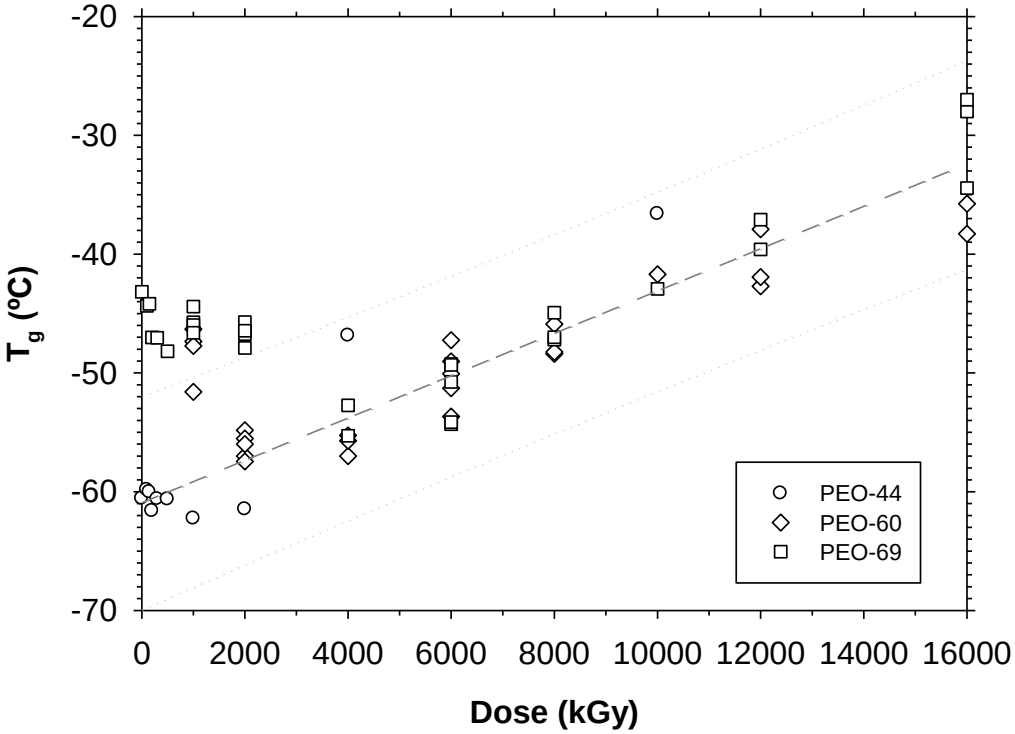


Figure 2. T_g vs dose for the copoly(ether-imide)s.

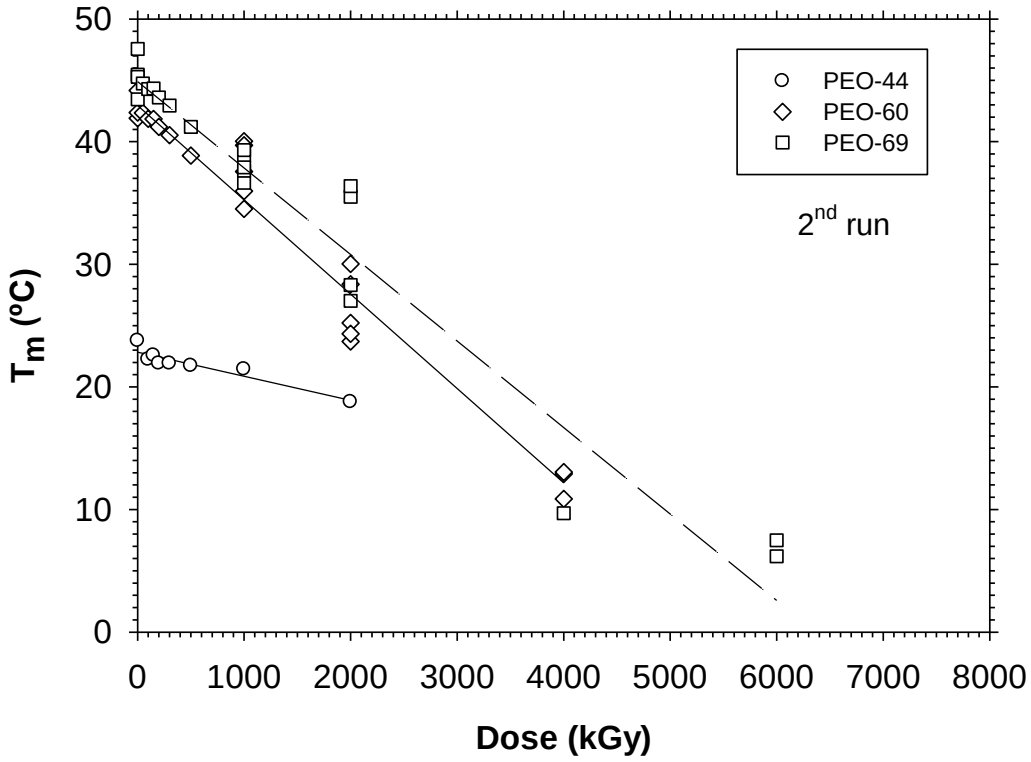


Figure 3. Maximum of the melting endotherm in the second heating run vs dose for the copoly(ether-imide)s.

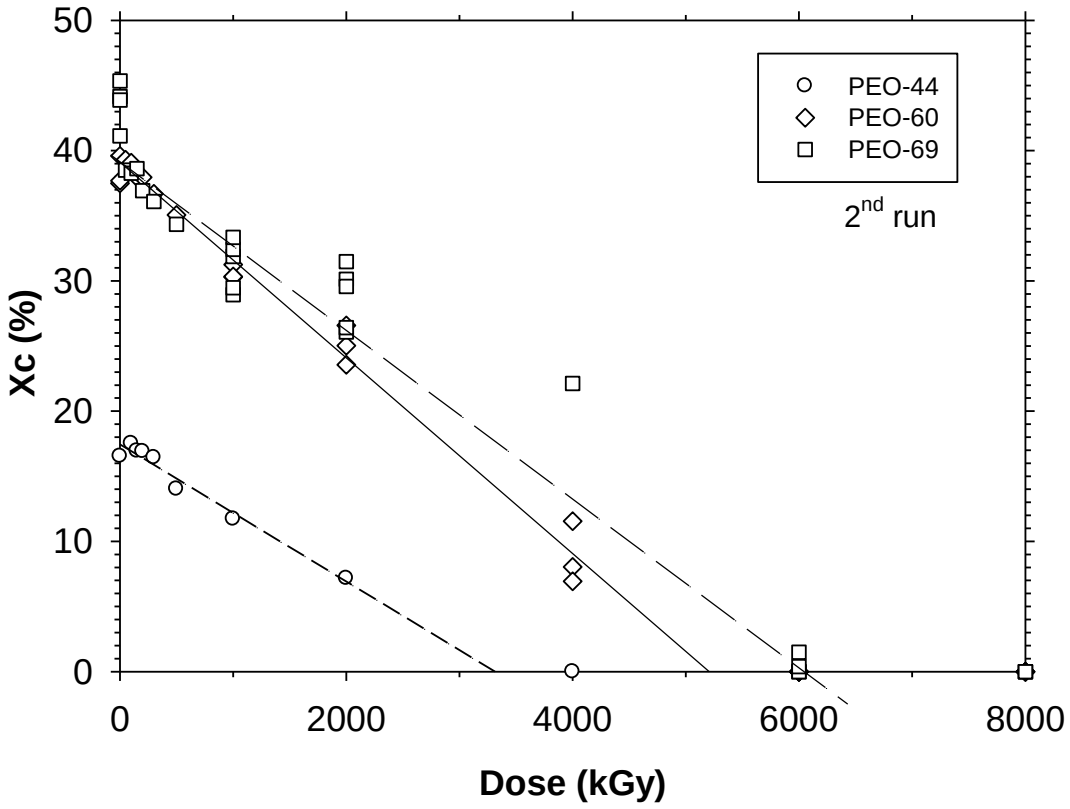


Figure 4. Percentage of crystallized PEO vs dose for the second heating run for the copoly(ether-imide)s.

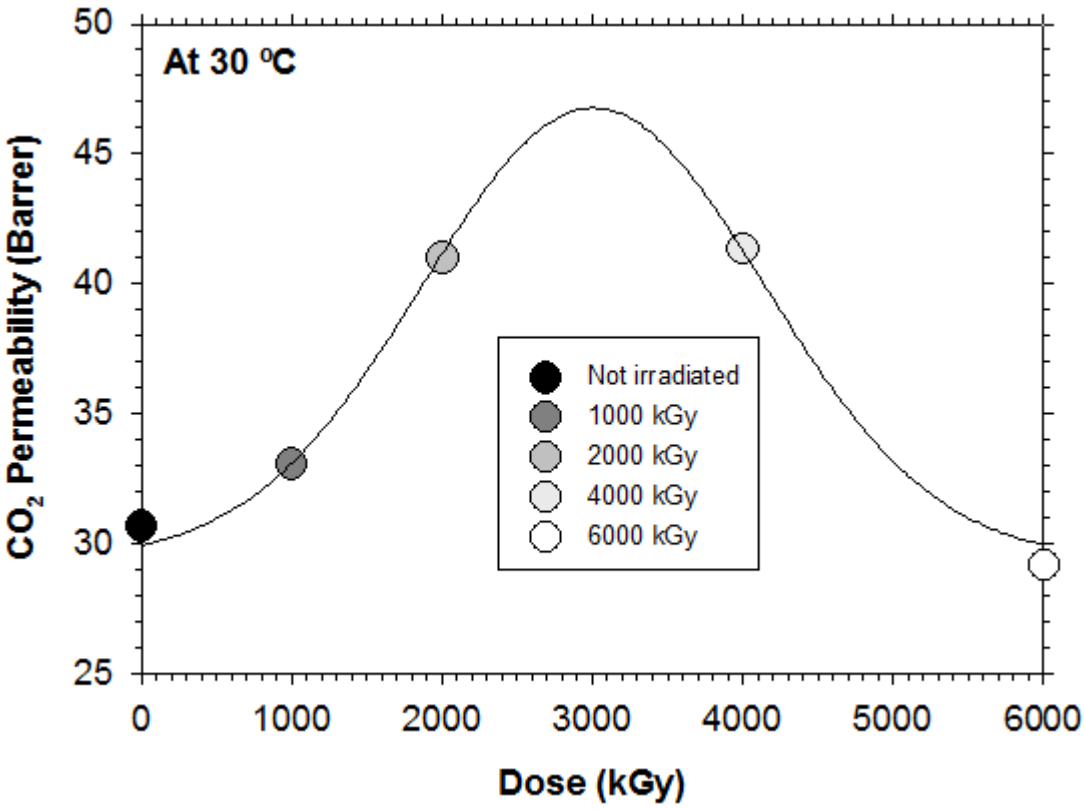


Figure 5. CO_2 permeability of the PEO-60 irradiated membranes as a function of absorbed dose measured at 30 ºC.

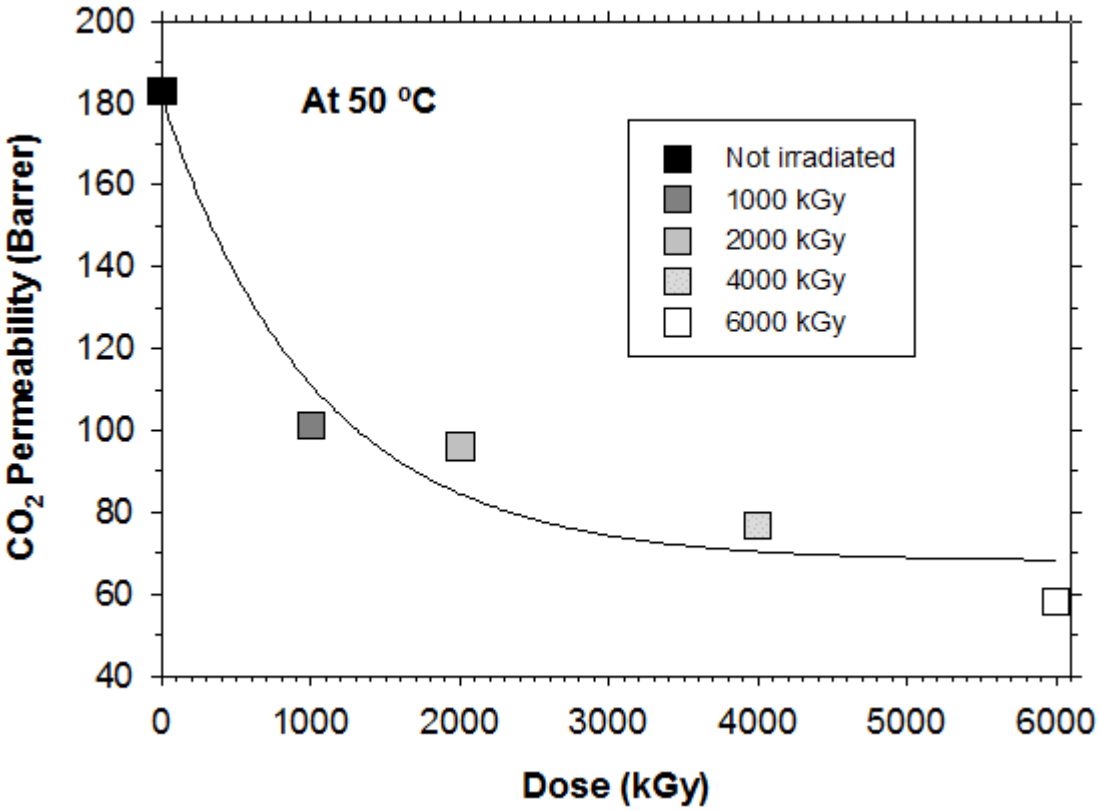


Figure 6. CO_2 permeability of the PEO-60 irradiated membranes as a function of absorbed dose measured at 50 ºC.

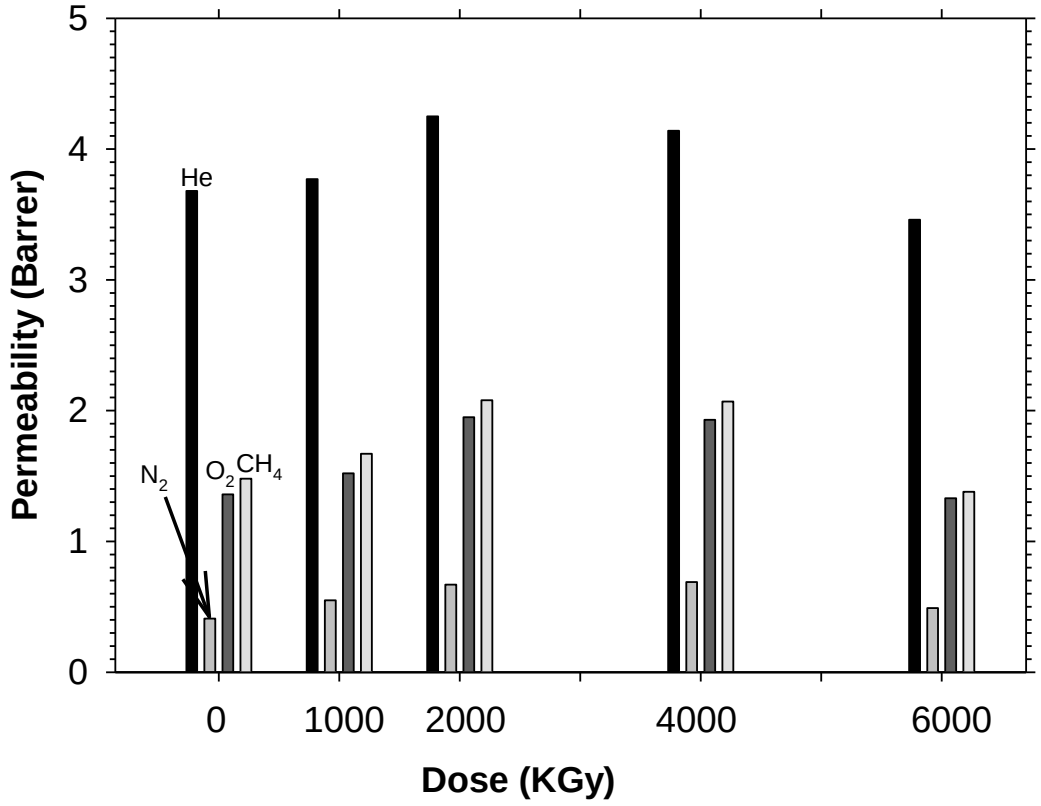


Figure 7. Permeabilities for other gases as a function of the absorbed dose for PEO-60.

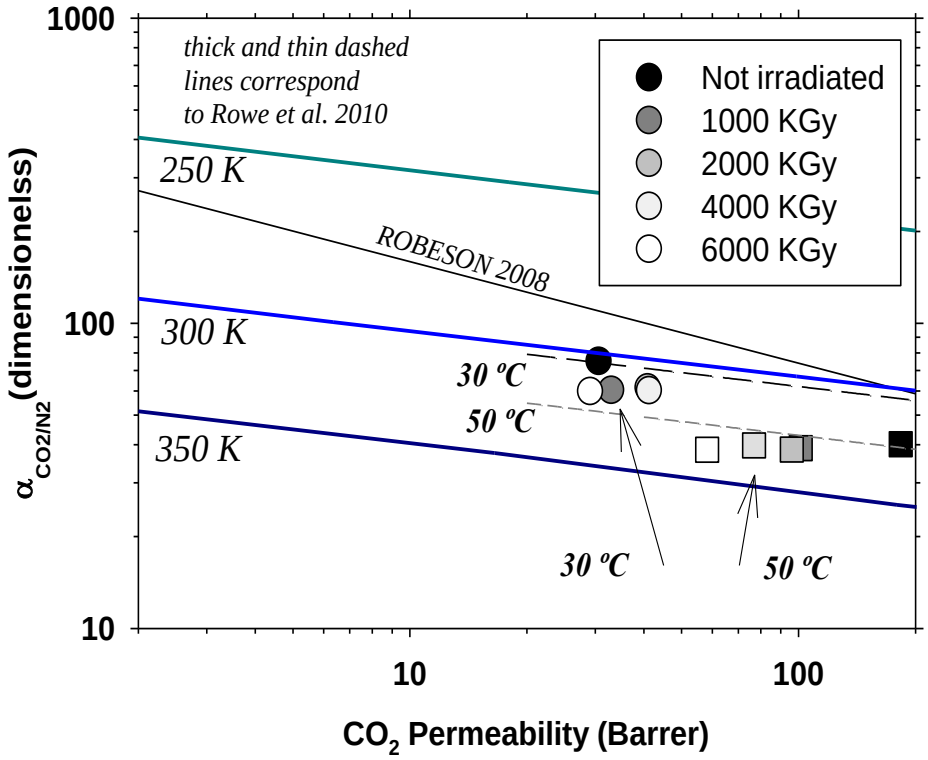


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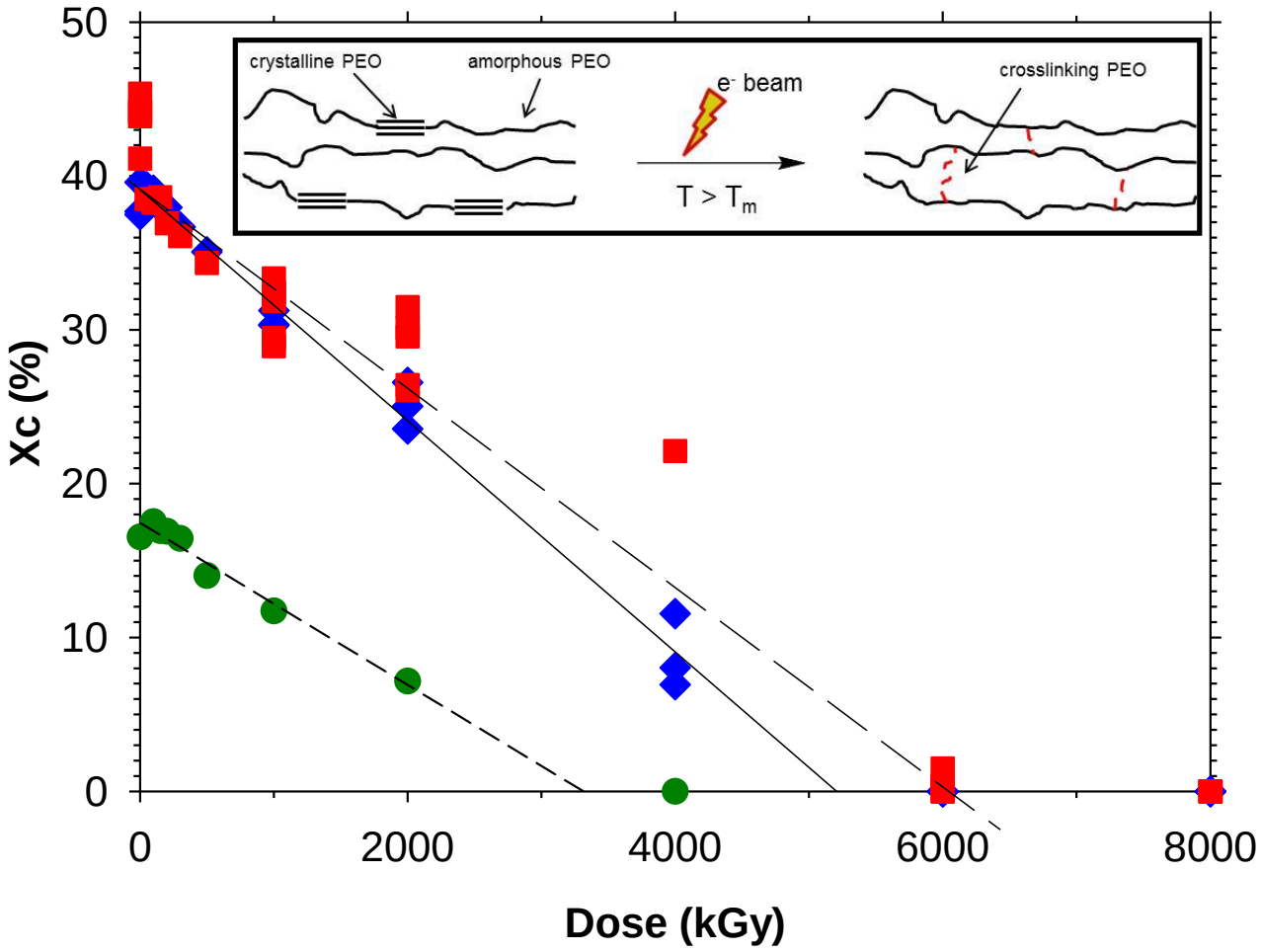
FIGURE FOR ToC_ABSTRACT



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